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# Flammability and Explosion Limits of H<sub>2</sub> and H<sub>2</sub>/CO: A Literature Review

Prepared by

N. COHEN

Space and Environment Technology Center  
Technology Operations

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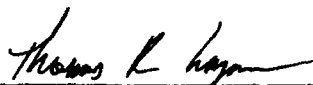
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\_\_\_\_\_  
THOMAS R. LAYNE, Lt, USAF  
Atlas Propulsion System Manager

  
\_\_\_\_\_  
RONALD D. GUTT, Capt, USAF  
Chief, Atlas Engineering

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## INTRODUCTION

If a volume of gas contains a fuel mixed with an oxidizer (and diluent), the possibility exists (if the conditions are appropriate) for auto-ignition, sustained combustion, detonation and/or deflagration. The purpose of this report is to review the conditions necessary or sufficient for any of these events to occur, as well as to define the usual terminology.

**Combustion.** The term "combustion" is usually used to describe a relatively rapid oxidation reaction between a fuel and an oxidizer that produces heat or radiant energy. Since reactions between stable molecules are generally slow at moderate temperatures, for all practical purposes a combustion process (which must be relatively rapid) requires the presence of chemically reactive intermediates—generally free radicals or ions.

**Chain reaction.** Any sustained combustion process requires a chain reaction: a repeating sequence of individual molecular processes that regenerates the active intermediates such as free radicals. A chain reaction consists of initiation, propagation, and termination steps, which, respectively, create, maintain, and destroy the reactive intermediates that are the chain carriers (henceforth assumed to be free radicals). The propagation steps can be simple (linear) or branching (quadratic), depending on whether the net number of chain carriers remains constant or increases in the course of that step.

**Explosion.** From the viewpoint of chemical kinetics, an explosion occurs when the rate of reaction in a reacting mixture increases with time without limit, until either the fuel or oxidizer is consumed or nearly so. This increase in reaction rate can be a consequence simply of increasing temperature in an exothermic reaction (*thermal explosion*), or of a chain branching reaction (*branched chain explosion*). In the former case, e.g., the reaction between hydrogen ( $H_2$ ) and chlorine ( $Cl_2$ ), there are no chain branching reactions, but exothermic steps heat the reacting mixture, which accelerates those same steps, and the overall reaction rate increases continuously, until limited by consumption of one of the reagents. In a branched chain reaction, acceleration is possible even without self-heating because the nature of the chemical steps increases the concentration of the free radical intermediates steadily. Whether or not an explosion will occur is determined by chemical kinetics: that is, the rates of the various gas-phase (and possibly surface) reactions.

**Initiation.** Some source of energy is necessary to initiate a chain reaction. Some chain reactions can be initiated by a stray photon, charged particle, cosmic ray, or other inadvertent energetic source. This is often regarded, in casual parlance, as a *spontaneous* reaction. Intentional initiation can be the result of a spark (as in an internal combustion gasoline engine), flash lamp, or laser illumination. Initiation can also occur more or less uniformly throughout a mixture as a result of gradual heating and/or compression (as in a diesel engine).

**Auto-ignition.** Auto-ignition describes the phenomenon of a spontaneous ignition of a fuel/oxidizer mixture under the prevailing conditions of pressure, temperature, composition, and enclosure. (The latter refers to the nature of the container, if any: volume, volume/surface ratio, nature of surface.) If spontaneous ignition ensues immediately upon mixing the fuel and oxidizer (at room temperature or below), the combustion reaction (and the mixture) is said to be *hypergolic*.

**Detonation or deflagration.** When reaction is initiated at a localized ignition source, there is the possibility of propagation of a combustion wave through the mixture. Such a wave is called a detonation or deflagration, gas-dynamic characterizations respectively designating a combustion wave that is supersonic or subsonic. In normal use, a deflagration is the same as a (subsonic) flame. An explosion need not be a detonation because it doesn't require the passage of a combustion wave. On the other hand, a detonation can occur under conditions that are ordinarily not considered explosive. (What happens is that the localized deposition of energy makes a small volume of mixture explosive, and the chemical energy liberated can progressively propagate into adjacent volumes of gas.) Whether a detonation will occur depends on gas-dynamic characteristics of the medium of interest, including the rate of chemical heat release. For example, a mixture of hydrogen and oxygen at room temperature (or even as hot as  $390^{\circ}\text{C} = 663\text{ K}$ ) and 1 atm pressure is not considered explosive (see Figure 1): it will remain stable for an indefinite period of time. However, if a small spark occurs, the local exothermic reaction can initiate a combustion wave that shock-heats adjacent gas to a temperature and/or pressure sufficient for sustained chain branching reaction—i.e., explosion. This type of explosion is a detonation. Explosions, deflagrations, or detonations are different consequences of ignition. It is worth stressing that mixtures regarded as nonexplosive (i.e., not spontaneously explosive) can nevertheless detonate if suitably initiated.

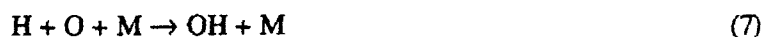
**Flammability and explosion limits.** Explosion limits separate spontaneously explosive from non-spontaneously explosive conditions—commonly on a pressure vs temperature curve for a given gas mixture. Each mixture composition (e.g., relative fuel : oxidizer : diluent) in a given container will have its own explosion limits. The locus of these limits is determined experimentally, but a knowledge of the chemical kinetics of the mixture can approximately predict the limits. Flammability (or deflagration) limits define the extreme compositional limits that will support a flame if an external ignition is provided. Flammability limits for a specific fuel-oxidizer-diluent combination depend on initial temperature, pressure, and nature of diluent(s) (if any). Detonation limits demark the range of conditions under which a deflagration in a gas can transform to a detonation. Gas-dynamic considerations will determine whether the shock wave generated by initiation can lead to explosion; it may turn out that (perhaps contrary to intuition) as the shock strength increases (i.e., as Mach number increases), it reaches a magnitude too large to cause detonation. A gas sample does not need to be completely enclosed for detonation to occur, although most

discussions of detonability presume a cylinder closed at one end. For further discussion, see Glassman<sup>1</sup> and Kuo<sup>2</sup>.

## HYDROGEN (H<sub>2</sub>) COMBUSTION

Figure 1 shows the explosion limits of a stoichiometric mixture of hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>). (The term, "stoichiometry" is often used to refer to the relative proportions of reagents; more specifically, a "stoichiometric mixture" is one in which the relative proportions of reagents are such that complete reaction will consume all reagents entirely. A stoichiometric mixture of H<sub>2</sub> and O<sub>2</sub> contains the two species in a 2:1 molar ratio.) The curve shows that at any temperature between 400° and 580°C, as the pressure is increased from a very small value, the mixture passes from a non-explosive (I) to an explosive (II) to a nonexplosive (III) to an explosive (IV) regime. The explanation of these limits lies in the detailed kinetics of the H<sub>2</sub>-O<sub>2</sub> reaction mechanism.

The H<sub>2</sub>-O<sub>2</sub> reaction is the classic example of a chain reaction with branching. The essential steps in the mechanism are:





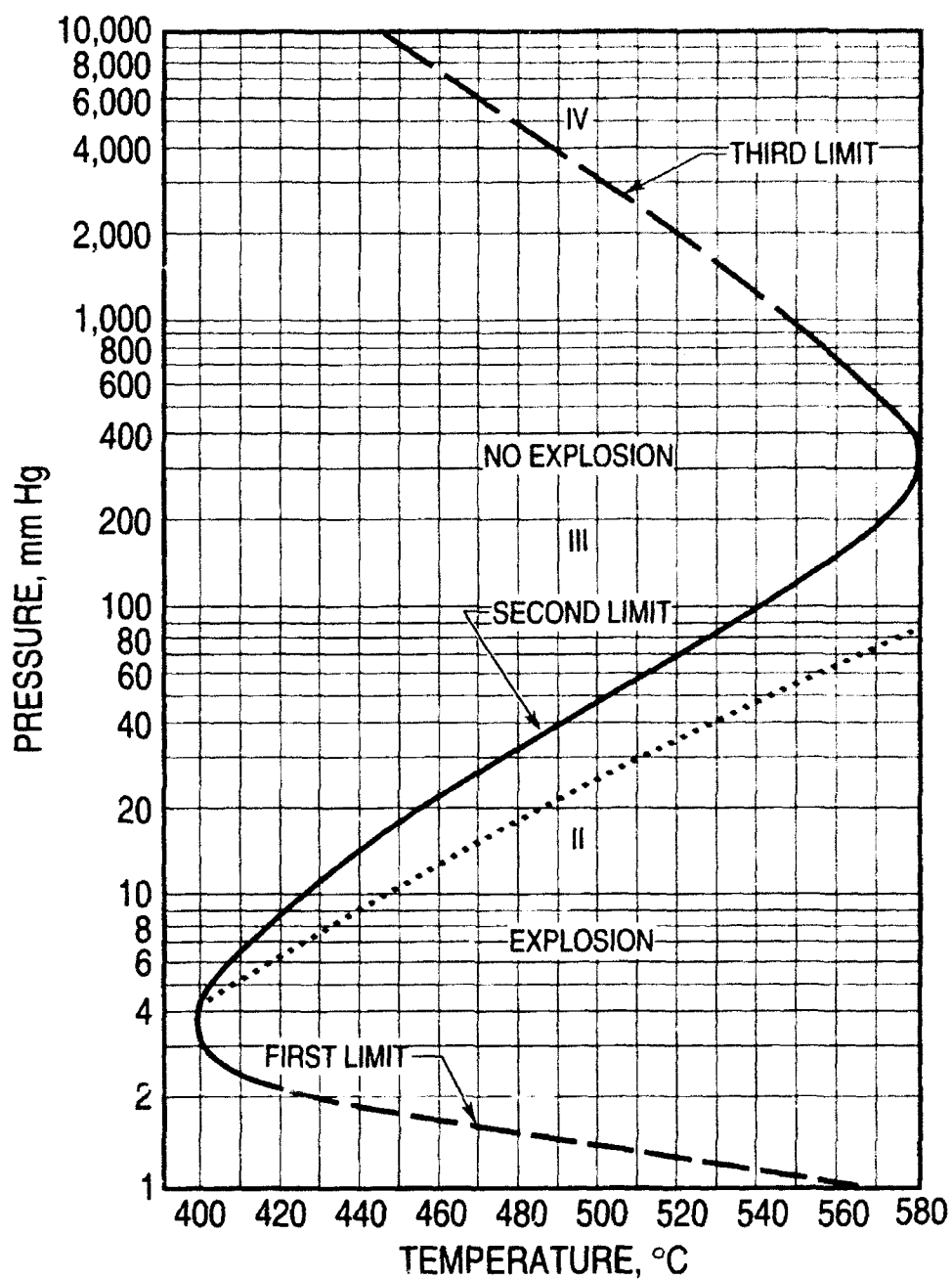


Figure 1. Explosion limits of stoichiometric  $H_2-O_2$  mixture in a spherical KCl-coated vessel of 7.4 cm diameter. First and third limits are partly extrapolated. Dotted line defines condition where  $2k_2 = k_{10}[M]$  in stoichiometric  $H_2-O_2$ . (From Ref. 3.)

Reaction (1) represents the initiation step. Dissociation of  $H_2$  is the most likely initiation, but dissociation of  $O_2$  would be equally effective. Once H (or O) atoms are produced, they continue to react via the propagation steps (2-4). Two of these (2 and 3) are chain branching, since H, O, and OH are all effective chain carriers. Competing with the chain propagation steps are the termination steps, which remove chain carriers (5-9). In these reactions, M can be any gas phase molecule, but the reaction rate coefficient will depend on the nature of M. In any case, its function is simply to remove excess energy—otherwise the colliding reagents would simply redissociate without any net change. Reactions (9) and (11) are not elementary steps, like the others, but represent a sequence of events at the wall: probably the successive sticky collisions of two atoms or radicals. A branched chain reaction will almost always lead to an explosion because the propagation rates will eventually overtake the termination rates. A chain reaction without branching will become explosive only if propagation rates increase faster than termination rates with rising temperature.

Region I of Figure 1 is defined by the condition that reactions (9) occur faster than propagation steps, so that there is no monotonic increase in total chain carrier concentration. The location of the first limit can vary considerably with the nature of the wall material, or with the dimensions of the container. Lewis and von Elbe<sup>3</sup> provide data on the effects of these parameters on the first limit. As pressure increases, the diffusion rates to the walls decrease, and eventually a pressure is reached at which propagation and termination rates are equal. This defines the first explosion limit. Experimentally, it is very difficult to establish the limit, since it is sensitive to the shape and size of the reaction vessel and the nature of the wall, and may even change as successive experiments are carried out in the vessel. At higher pressures (Region II), propagation rates outrun wall termination. However, as pressure increases, reaction (10), the rate of which varies approximately as  $p^2$ , increases in relative importance until its rate is large enough to outweigh the propagation reactions. This defines the second explosion limit: at pressures just above this limit (Region III), reaction (10) is responsible for preventing explosion. The dotted line on Figure 1 defines the conditions at which  $2k_2 = k_{10}[M]$  in stoichiometric  $H_2/O_2$ . When  $2k_2/k_{10}[M]$  exceeds unity, the net production of chain carriers exceeds destruction; if reaction (12) did not occur, this should coincide with the 2nd limit. Since the value of  $k_{10}$ , the rate coefficient for (10), depends on the nature of the gas M, the second limit will move down in a diluent which is more efficient than stoichiometric  $H_2/O_2$  at facilitating  $H + O_2$  combination. Based on reactions (1-10),  $HO_2$  is an inert product of reaction, whose only fate is wall destruction (11) to give  $H_2$  and  $O_2$ . As pressure continues to increase (Region IV), conditions are reached such that reaction (12) becomes important; this converts  $HO_2$  from an inert species into a chain carrier, and the mixture can again become explosive. The third explosion limit is defined by the condition that reaction (12) is fast enough to prevent  $HO_2$  from building up.

Above 580°C (for the conditions of Figure 1; for other surfaces, or in diluents, or at other mixture ratios, this limit will vary), all conditions of  $p$  and  $T$  lead to explosion; this is the result of temperature on the reaction rates. In general, termination reactions such as (5-11) have rate coefficients with very small or even negative temperature dependences, while those of propagation reactions are usually positive, though not very large. (Initiation reactions generally have large positive temperature dependences.) For these reasons, as  $T$  increases, the condition will usually be reached when the propagation reactions outrun the termination reactions, and the mixture will be explosive no matter what the pressure.

In trying to predict explosive behavior, it is important to bear in mind the factors that are responsible for the different explosion limits. Thus, for example, a code such as SPF III, which as presently constituted considers only homogeneous gas phase reactions, cannot be used to predict explosions if the first explosion limit is the determining factor.

### CARBON MONOXIDE (CO) COMBUSTION

The nature of the mechanism of pure CO-O<sub>2</sub> combustion is not so well understood as that of H<sub>2</sub>-O<sub>2</sub>. In pure CO-O<sub>2</sub>, the initiation step has been presumed to be



Semenov proposed that this was followed by "energy branching"--steps involving formation and reaction of highly energetic (*e.g.*, vibrationally excited) CO<sub>2</sub>:



but this hypothesis has not been verified. In fact, the nature of the successive steps has resisted elucidation, and there is growing evidence that completely pure ("dry") CO-O<sub>2</sub> will not explode. (Only 20 ppm of hydrogen are sufficient to ensure the "wet" reaction.) In the presence of OH radicals, a much faster initiating step is



H radicals would then terminate by the same processes as in the hydrogen-oxygen case. Thus, the first and second explosion limits in "moist" CO-O<sub>2</sub> should be very similar to those in H<sub>2</sub>-O<sub>2</sub>. There is, however, the possible complication of reaction of HO<sub>2</sub> with CO:



Conceivably this could lead to a third explosion limit, something that has not been observed.

Unless scrupulous efforts were made to remove H<sub>2</sub>O and any organic vapors (e.g., from pump oil or greases), experimental measurements in reality studied the reaction in the presence of traces of hydrogenous species. These are also the conditions of most interest for the purposes of this review.

### FLAMMABILITY LIMITS: H<sub>2</sub>-O<sub>2</sub>-DILUENT

H<sub>2</sub> flammability limits depend on %H<sub>2</sub>, %O<sub>2</sub>, diluent, T, and p. Any diluent will cause the upper and lower flammability limits to narrow and eventually approach one another. Lowering pressure substantially below atmospheric generally does the same. The relative efficiencies of different diluents at narrowing the flammability limits vary from fuel to fuel, and sometimes even for the same fuel, depending on the conditions of the experiment. The limits (without diluents) also depend on the configuration of the experiment: whether the flame is propagating upward, downward, or horizontally (see Table 1). The relevance of this factor is great when one is concerned with the possible flammability of hydrogen in burners, tubular reactors, or transport pipes, and most early experiments must have been conducted with these applications in mind. Another application would be to gases in large, possibly enclosed, volumes. For safety purposes, we should assume the most lenient requirements. For H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at T<sub>0</sub> = 298 K and p<sub>0</sub> = 1 atm, there are well-defined data that delineate the flammable region as a function of composition. These are shown in Figure 2 (taken from Fig. 7 of Coward and Jones.<sup>4</sup>). This widely copied figure does not present the data in the most useful manner for some applications. The two intercepts of the boundaries of the flammable region with the ordinate are the flammability limits for a pure H<sub>2</sub>-air mixture. As the air is diluted with CO<sub>2</sub> or N<sub>2</sub>, the upper flammability limit is lowered, until finally at 75% diluent (in the case of N<sub>2</sub>) the limits meet; at higher diluent concentrations the mixture is not flammable. The abscissa at the top of the graph shows the percent of O<sub>2</sub> that results as the diluent concentration is added; it decreases from 21% (pure air) to zero. The graph also shows the locus of stoichiometric mixtures.

As T<sub>0</sub> increases, the flammability limits widen; see Figure 3 (taken from Fig. 6 of Coward and Jones). From these latter data, one can calculate the following expressions for the upper and lower (downward) flammability limits as functions of T in K, where Lim is in units of %H<sub>2</sub> in air:

$$\text{Lim}_{\text{lower}}(\text{H}_2) = -0.0080 T + 11.68 \quad (\text{I})$$

$$\text{Lim}_{\text{upper}}(\text{H}_2) = 0.0275 T + 63.24 \quad (\text{II})$$

Table 1. Flammability Limits of H<sub>2</sub> in Other Gases<sup>8</sup>

Gas	Lower limit % H <sub>2</sub>	Upper limit % H <sub>2</sub>	Experiment
O <sub>2</sub> /N <sub>2</sub> (21:79)	4.19	74.6	Upward propagation, open tube
O <sub>2</sub> /N <sub>2</sub> (21:79)	9.0		Downward propagation, open tube
O <sub>2</sub> /N <sub>2</sub> (21:79)	9.4	64.8	Closed globe, side ignition
O <sub>2</sub> /He(22:78)	7.72	75.7	Upward propagation, open tube
O <sub>2</sub> /Ar(21:79)	3.17	76.4	Upward propagation, open tube
N <sub>2</sub> O/N <sub>2</sub> (21:79)	4.19	29.0	Upward propagation, open tube
O <sub>2</sub> /CO <sub>2</sub> (21:79)	5.31	69.8	Upward propagation, open tube
O <sub>2</sub> /CO <sub>2</sub> (21:79)	13.1		Downward propagation, open tube
O <sub>2</sub> /CO <sub>2</sub> (21:79)	11.9	68.2	Closed globe, side ignition

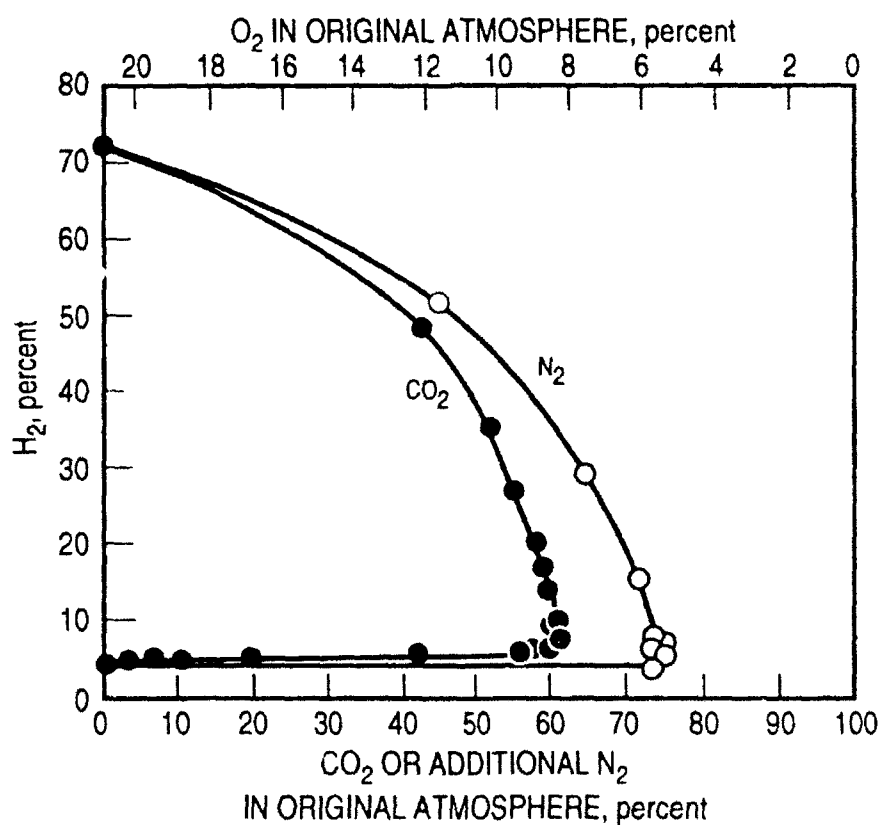


Figure 2. Limits of flammability of H<sub>2</sub> in air and CO<sub>2</sub> or N<sub>2</sub>. (From Ref. 4.)

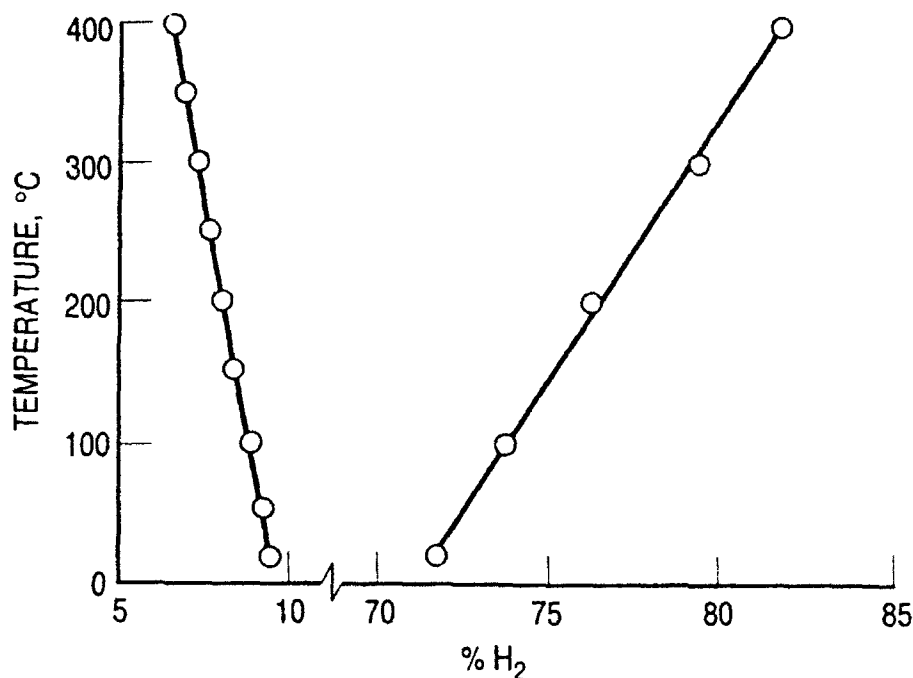


Figure 3. Influences of temperature on limits of flammability of  $H_2$  in air (downward propagation of flame). (From Ref. 4.)

However, a conceptually more revealing picture is obtained by regraphing these data so that the abscissa is total diluent. In the case of  $H_2$ - $O_2$ - $N_2$  mixtures, this results in Figure 4 (taken from De Soete<sup>5</sup>), showing the flammability limits for  $H_2$  in mixtures of  $N_2$  and  $O_2$  at 1 atm and at various temperatures. These results were obtained by filling a cylindrical cell with a given mixture, waiting a specified time to allow thorough mixing, and then sparking with 25 joules of energy. As De Soete points out, the flammability limits depend on the residence time: this results from slow pre-ignition reactions that generate  $H_2O$  while slowly consuming fuel. Ideally, one is interested in flammability limits at zero residence time, but this is experimentally unmeasurable. De Soete's data refer to 1 sec residence time, which is probably short enough to be considered zero residence time. However, the narrowing of the flammable region at the highest temperatures (823 and 847 K) is probably an artifact of the finite residence time because, at such high temperatures, pre-reaction is increasingly significant, producing  $H_2O$ , which narrows the flammability limits (see below). Since  $\%H_2 + \%N_2 + \%O_2 = 100$ , the region to the right of a diagonal line connecting the two 100% coordinates is physically meaningless; and diagonals connecting 90%  $H_2$  with 90%  $N_2$  (or 80%  $H_2$  with 80%  $N_2$ , etc.) are lines of constant percentage  $O_2$ . Presented in this way, the graph shows that the upper limits lie on lines of constant  $O_2$ . It is apparent that most of the composition space is in the flammable region, even at temperatures as low as 298 K. By 689 K, the upper limit of  $O_2$  is only about 1%. Also on this figure

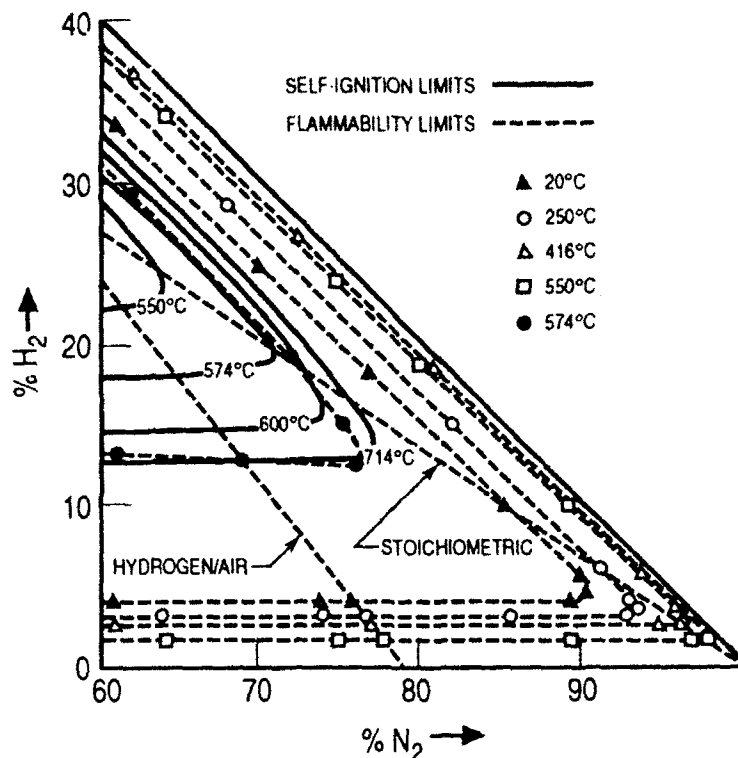


Figure 4. Flammability limits at residence time of 1 sec and self-ignition limits of  $\text{H}_2/\text{O}_2/\text{N}_2$ . (From Ref. 5.)

are De Soete's limits of auto-ignition for  $\text{H}_2\text{-O}_2\text{-N}_2$  at 823, 847, 873, and 987 K. Coward and Jones presented flammability limits for  $\text{H}_2$ ,  $\text{CH}_4$ , or  $\text{CO}$  in air diluted by  $\text{N}_2$  or  $\text{CO}_2$  in another format that may also be useful; their Fig. 1 is reproduced in Figure 5. The y-intercepts give flammability limits for fuel-air; as one moves to the right in the figure, one sees how the limits narrow with increasing added diluent.

The flammability limits also vary with pressure. Figure 6 (from Coward and Jones) shows the effect of pressure on the flammability limits of  $\text{H}_2\text{-O}_2$  from 1 to 220 atm. Holmstedt<sup>6</sup> presented data showing the maximum safe concentration of  $\text{O}_2$  (*i.e.*, the upper limit) in various  $\text{H}_2\text{-O}_2\text{-He}$ ,  $\text{H}_2\text{-O}_2\text{-Ar}$ ,  $\text{H}_2\text{-O}_2\text{-Ne}$ ,  $\text{H}_2\text{-air}$ , and  $\text{H}_2\text{-O}_2\text{-CO}_2$  mixtures at pressures up to 30 atm. His graph for  $\text{H}_2\text{-O}_2\text{-He}$  mixtures is reproduced in Figure 7. At subatmospheric pressures, the limits vary negligibly for  $p$  from 1 atm down to about 6 torr. Figure 8 shows the pressure dependence at lower pressures.<sup>7</sup>

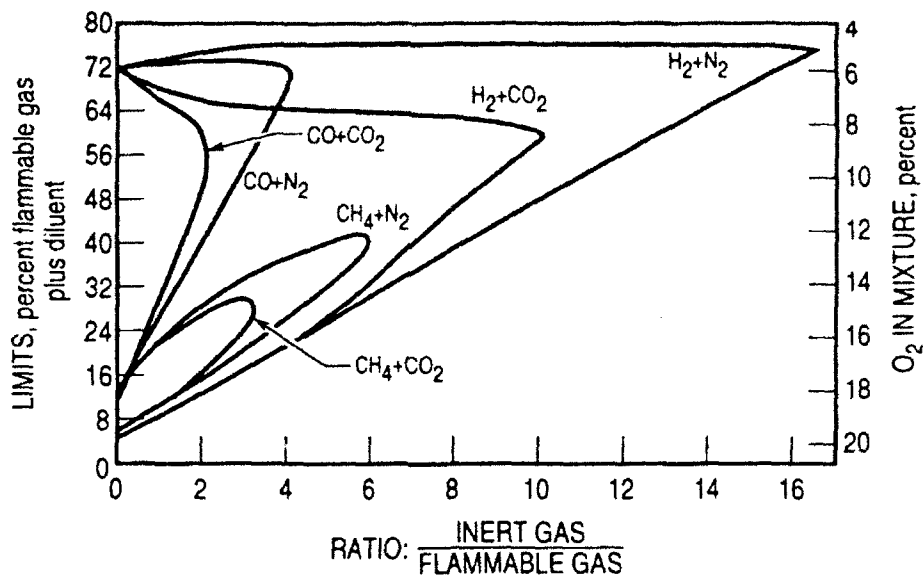


Figure 5. Limits of flammability of  $H_2$ ,  $CO$ , and  $CH_4$  containing various amounts of  $CO_2$  and  $N_2$ . (From Ref. 4.)

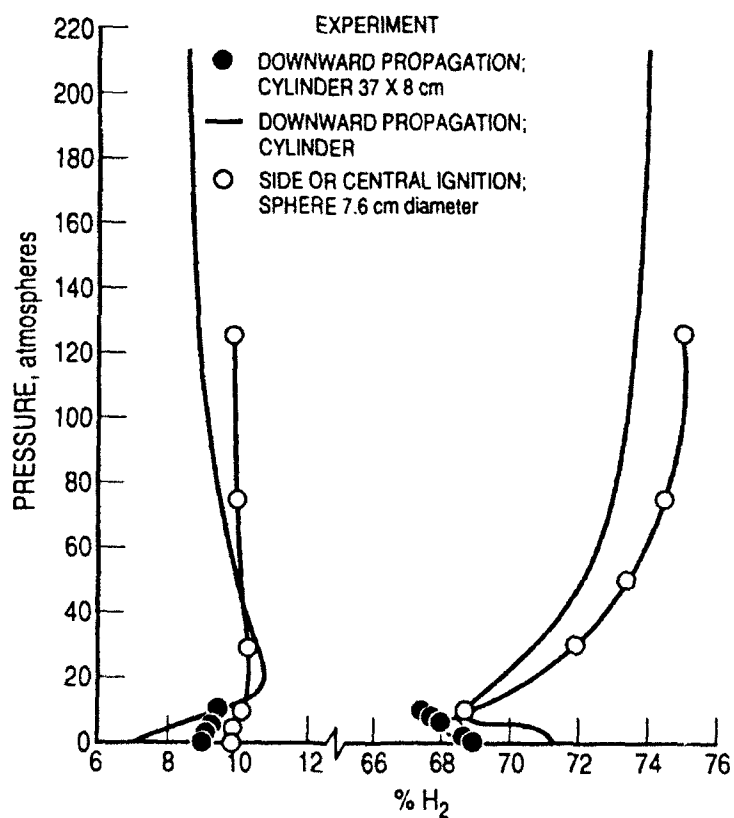


Figure 6. Effect of pressures above normal on limits of  $H_2$  in air. (From Ref. 4.)



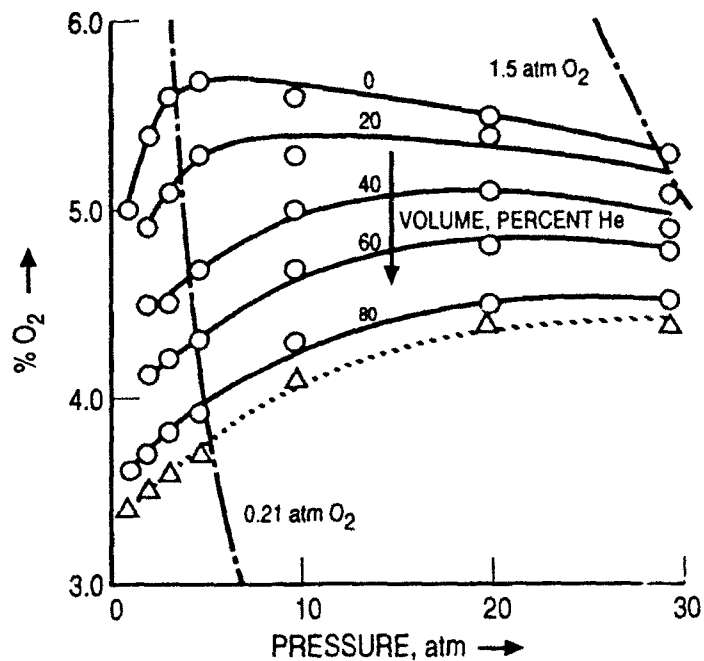


Figure 7. The upper limit of flammability of  $\text{H}_2/\text{O}_2/\text{He}$  mixtures of 0, 20, 30, 60, and 80% helium concentration at elevated pressures. --- maximum safe percentage of oxygen. ---- isobars showing partial pressures of oxygen of 0.21 and 1.5 atm.. (From Ref. 6.)

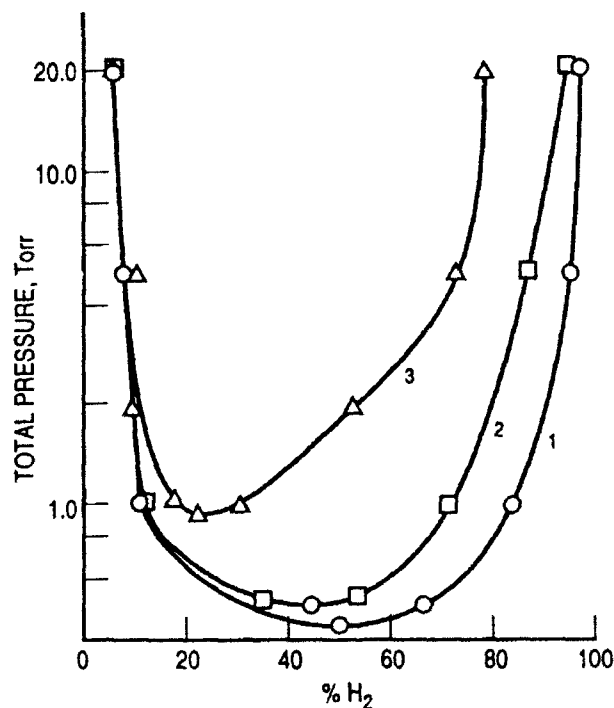


Figure 8. Flammability limits below 20 mm Hg total pressure. 1,  $\text{H}_2\text{-O}_2$ ; 2,  $\text{H}_2\text{-air}$ ; 3,  $\text{H}_2\text{-O}_2\text{-N}_2$  (60/40  $\text{O}_2/\text{N}_2$ ). (From Ref. 7.)

Different diluent gases reduce the flammability limits to differing degrees, as shown in Table 1. Experiments with H<sub>2</sub>-air mixtures standing over water at various temperatures showed that as T increases, and partial pressure of H<sub>2</sub>O increases accordingly, the upper limit falls rapidly and the lower limit rises slowly. With 60% H<sub>2</sub>O present (359 K), the limits are equal at about 10% H<sub>2</sub>.

Figures are given for both upward and downward propagation in order to show the type of variability the limits exhibit under different conditions. In the case of the N<sub>2</sub>O/N<sub>2</sub> mix, the nitrous oxide is playing the role of the oxidant. Since problems of practical concern will very likely correspond to neither extreme, it is best to assume the widest flammability limits to ensure safety.

### DETONATION LIMITS OF H<sub>2</sub> IN O<sub>2</sub> OR AIR

Belles has developed a theory for predicting the detonation limits of H<sub>2</sub> in O<sub>2</sub> or air.<sup>9</sup> Detonation limits are typically expressed as the composition limits (fuel lean and fuel rich limits) for which a fuel-oxidizer at a given starting temperature and pressure, suitably initiated, will detonate. Kuo<sup>2</sup> recapitulates the theory, which is somewhat tedious to apply. The criterion for detonation is that the heat of combustion exceeds the enthalpy increase associated with the shock wave passing through the gas. The solution requires calculating a critical Mach number, which is a function of the rate of the chain branching step, initial temperature and pressure, and  $\gamma$  of the gas (ratio of  $C_p/C_v$ ). The enthalpy rise across the shock,  $\Delta h_s$ , determined by the temperature rise and average heat capacity, must be smaller than the enthalpy of combustion,  $\Delta h_c$ , determined by the chemistry. If a shock sufficient to bring the gas into the explosion region of Figure 1 (Region II) is not so strong that  $\Delta h_s$  exceeds  $\Delta h_c$ , then detonation can occur. These two enthalpy quantities are calculated for four different conditions: H<sub>2</sub>-O<sub>2</sub> with  $p_0 = 1$  atm and  $T_0 = 300$  K; H<sub>2</sub>-O<sub>2</sub> with  $p_0 = 0.5$  atm and  $T_0 = 300$  K; H<sub>2</sub>-O<sub>2</sub> with  $p_0 = 1$  atm and  $T_0 = 600$  K; and H<sub>2</sub>-Air with  $p_0 = 1$  atm and  $T_0 = 300$  K. The results are given in Table 2. (See Figure 9 for the first of these conditions.) To reiterate a point already alluded to: comparison with Figure 1 shows that although these mixtures can detonate if the fraction of H<sub>2</sub> falls within appropriate limits, all stoichiometric mixtures (and, *a fortiori*, any other compositions) with  $p_0 = 1$  atm and  $T_0 = 300$  K lie outside the usual explosion limits.

### FLAMMABILITY LIMITS OF CO IN O<sub>2</sub> OR AIR

The discussion of flammability limits of carbon monoxide is similar to that of hydrogen, except that in general there are fewer experimental data available. The limits of CO are compared to those of H<sub>2</sub> in Table 3.<sup>10</sup>

Table 2. Detonability Limits of H<sub>2</sub> in O<sub>2</sub> or Air<sup>a</sup>

	Lean Limit, %H <sub>2</sub>		Rich Limit, %H <sub>2</sub>	
	Expt;	Theory	Expt;	Theory
H <sub>2</sub> in O <sub>2</sub> (300 K, 1 atm)	15	14	90	92
H <sub>2</sub> in O <sub>2</sub> (300 K, 0.5 atm)		12		93
H <sub>2</sub> in O <sub>2</sub> (600 K, 1 atm)		9		95
H <sub>2</sub> in Air	18.3	14	59	62

<sup>a</sup>Experimental data from Ref. 2, p. 277; theoretical results for first and last cases differ slightly there.

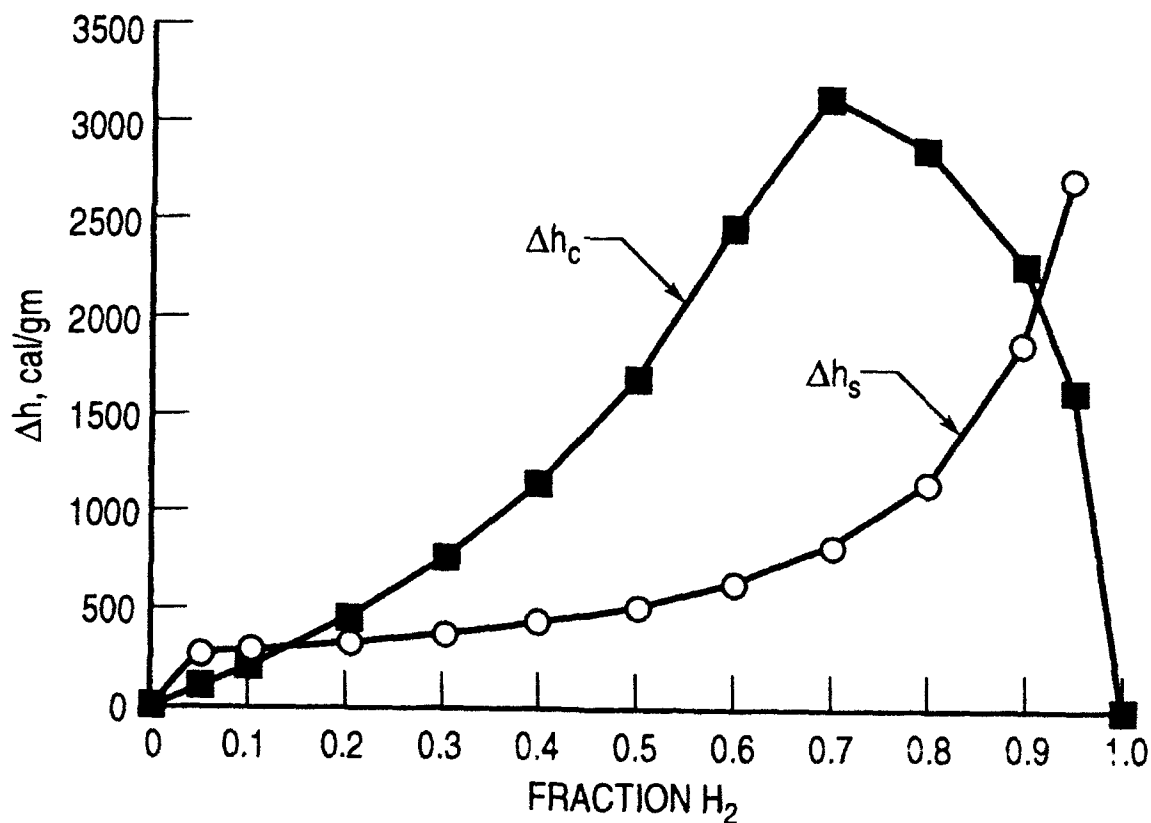


Figure 9. H<sub>2</sub>-O<sub>2</sub> detonation limits. T<sub>0</sub> = 300 K, p<sub>0</sub> = 1 atm H. ( $\Delta h_c$  and  $\Delta h_s$  are defined in the text.)

Table 3. Flammability Limits for CO and H<sub>2</sub>

Gas	Limits of air, %		Limits in O <sub>2</sub> , %	
	Upper	Lower	Lower	Upper
CO	12.5	74	15.5	94
H <sub>2</sub>	4.0	75	4.0	94

According to Table 3, the lower limits for H<sub>2</sub> in O<sub>2</sub> or air are equal, and the same is nearly true for CO. This is true in general; on the other hand, the upper limits are generally significantly higher in O<sub>2</sub> than in air. Figure 4 shows that the upper limit for H<sub>2</sub>-air depends only on the percent O<sub>2</sub> present and not on that of the N<sub>2</sub>; in H<sub>2</sub>-O<sub>2</sub>, if the H<sub>2</sub> is 94%, the O<sub>2</sub> is 6%. In H<sub>2</sub>-air, if H<sub>2</sub> is 75%, the O<sub>2</sub> is 21% of 25%, or 5.25%, and similarly for CO. In other words, in either air or pure oxygen, one must have at least 4-5% O<sub>2</sub> for either gas to burn.

As in the case of H<sub>2</sub>, the CO limits are dependent on both temperature and pressure. Increasing temperature tends to broaden the flammability range: *i.e.*, the lower limits decrease slightly and the upper limits increase slightly (less O<sub>2</sub> required). Experimental data are shown in Figure 10 (taken from Coward and Jones). An increase in pressure above 1 atm seems to have negligible effect on the H<sub>2</sub> flammability limits, as Figure 11 shows (from Coward and Jones). The dependence of the CO limits on pressure has not been well studied. The experiments cited by Coward and Jones on CO flammability at sub-atmospheric pressures suggest that, below a few hundred torr, CO is not flammable. At higher pressures this is not the case.

Figure 12 (from Coward and Jones) shows the effects on CO flammability limits if a diluent, either N<sub>2</sub> or CO<sub>2</sub>, is added to CO-air mixtures. The data for the case of additional nitrogen are replotted in Figure 13 with ordinates that will be more useful for many applications.

### FLAMMABILITY LIMITS OF CO-H<sub>2</sub> IN O<sub>2</sub> OR AIR

When two flammable gases are present, the flammability limits for the mixture can be calculated from a rule of LeChatelier (not the usual thermochemical principle).<sup>11</sup> According to this approximate relationship, the flammability limit of a mixture of two flammable gases is given by

$$\text{Lim} = 1/[f_1/L_1 + f_2/L_2],$$

where  $f_1$  and  $f_2$  are the mole fractions of the two flammable gases, not considering other gases (*i.e.*,  $f_1 + f_2 = 1$ ), and  $L_1$  and  $L_2$  are the limits of each gas alone. A similar expression generally applies to

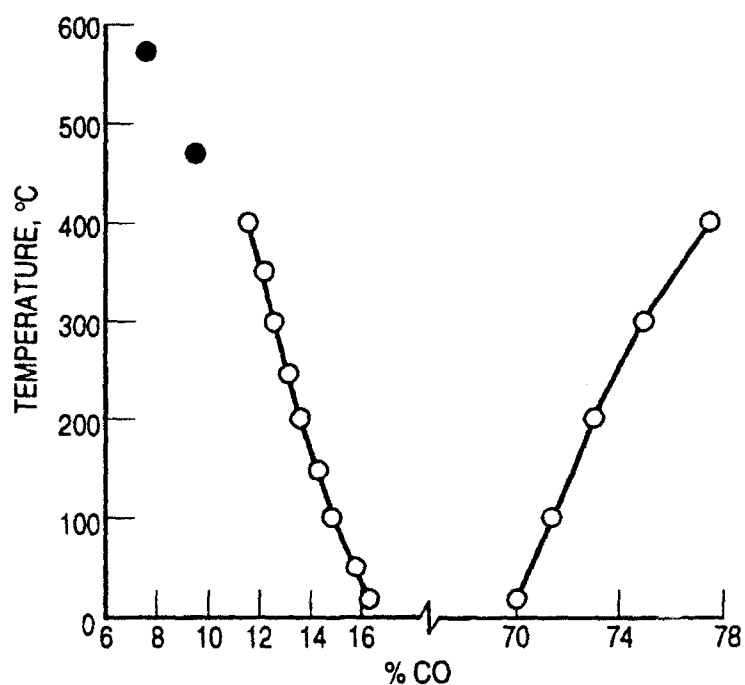


Figure 10. Limits of flammability of CO in air (downward propagation of flame), showing influence of temperature. (From Ref. 4.)

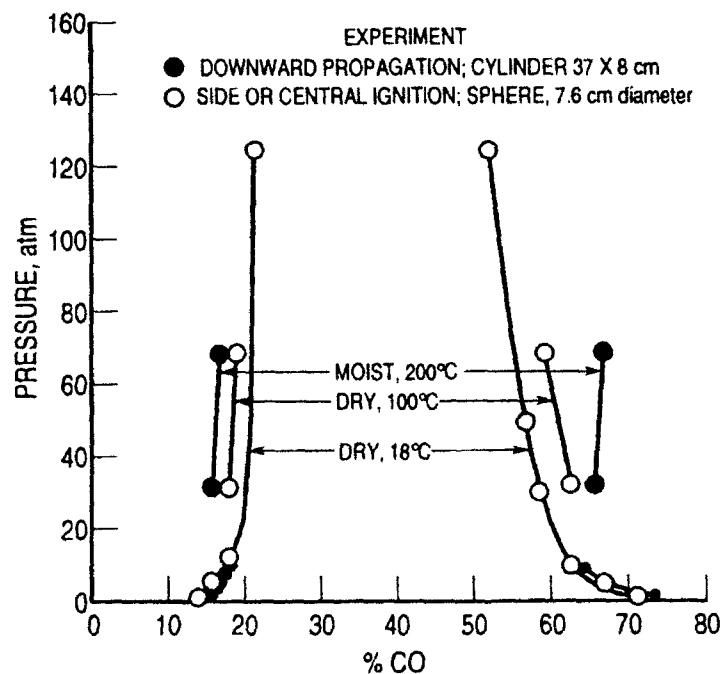


Figure 11. Effect of pressures above normal on limits of CO in air. (From Ref. 4.)

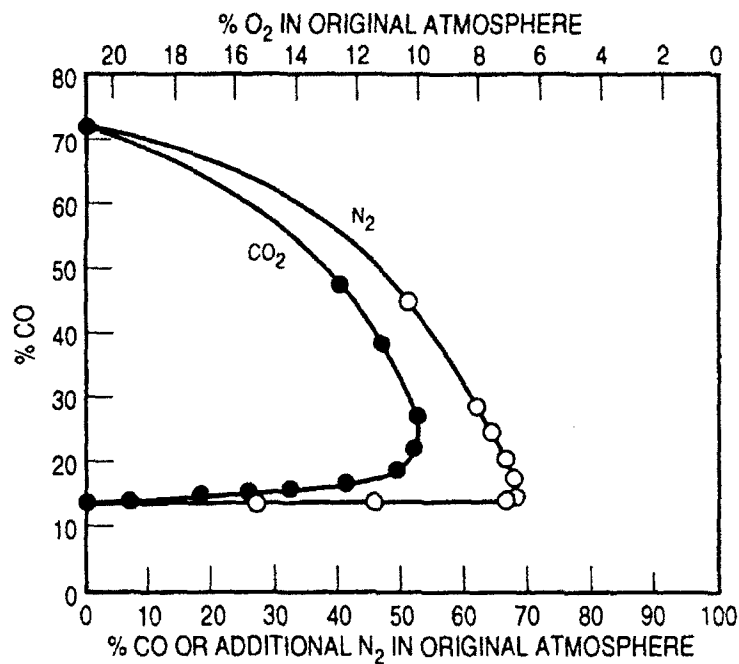


Figure 12. Flammability limits of CO in air and CO<sub>2</sub> or N<sub>2</sub>. (From Ref. 4.)

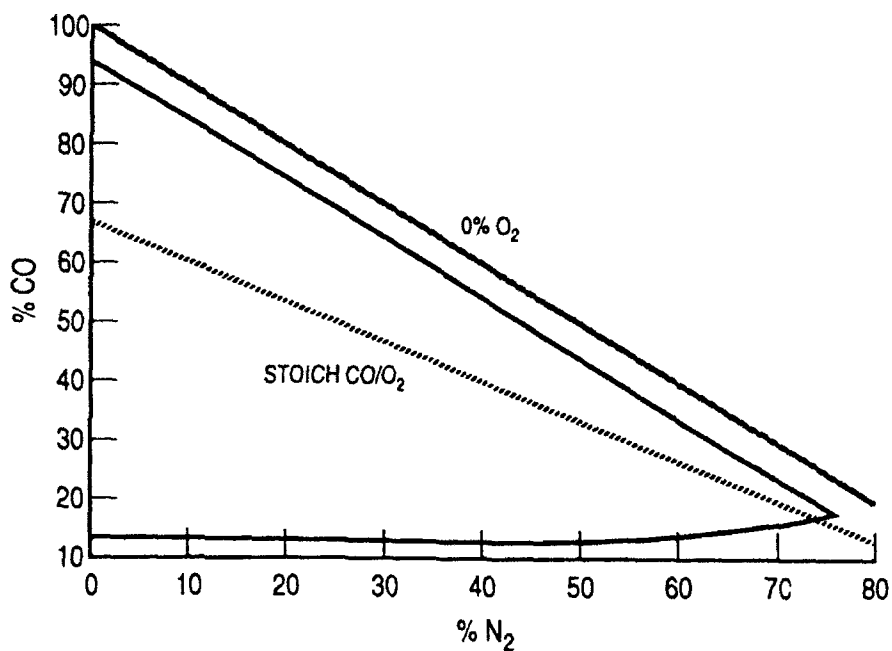


Figure 13. CO flammability limits-CO<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub>.

either upper or lower limits. This theoretical expression has been found to be approximately true for most common fuel gases, including H<sub>2</sub>/CO mixtures.<sup>12</sup> For example, what are the flammability limits of a mixture of 50:50 mixture of H<sub>2</sub>-CO in air? The lower limits for hydrogen in air and carbon monoxide in air are, respectively, L<sub>1</sub> = 0.125 and L<sub>2</sub> = 0.04. If f<sub>1</sub> = f<sub>2</sub> = .5, the lower limit for the mixture will be

$$\text{Lim}_{\text{lower}} = 1/[(.5/.125) + (.5/.04)] = .061,$$

or 6.1% mixture in air. Since the upper limits of CO and H<sub>2</sub> are nearly identical, the upper limit of any mixture will be the same as the limits of the individual components; i.e., Lim<sub>upper</sub> = L<sub>1</sub> = L<sub>2</sub>.

### COMPARISON OF FLAMMABILITY LIMITS OF VARIOUS FUELS

It is instructive to compare the limits of H<sub>2</sub> with those of other common fuels (Table 4) to see just how broad the limits are.

Table 4. Flammability limits of several fuels<sup>a</sup>

Gas	Limits in air, %		Limits in O <sub>2</sub> , %	
	Lower	Upper	Lower	Upper
Hydrogen	4.0	75	4.0	94
Carbon monoxide	12.5	74	15.5	94
Methane	5.3	14	5.1	61
Ethane	3.0	12.5	3.0	66
Propane	2.2	9.5	2.3	55
Butane	1.9	8.5	1.8	49
Hexane	1.2	7.5		
Iso-octane	1.1	6.0		
Benzene	1.4	7.1		
Methanol	7.3	36		
Ethanol	4.3	19		
Methyl ether	3.4	18		
Gasoline	1.4	7.6		
Natural gas	4	17		
Carbon disulfide	1.2	44		

<sup>a</sup>From Coward and Jones, Tables 44-45. Values refer to mole or volume percents.

### APPLICATION: ATLAS II AC-101 BOOSTER EXHAUST SYSTEM LEAK

Early in 1992, in an Atlas II test flight, a hot boattail anomaly occurred. It was hypothesized that a leak had developed in the booster exhaust system, resulting in the mixing of hot exhaust gases. For RP-1 fuel, the exhaust would consist primarily of 25% H<sub>2</sub>, 32% CO, and smaller quantities of CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, and other hydrocarbons mixing with ambient air. The question arose whether there was any chance of the

exhaust gases burning as a result of admixture of air. Two SPF III (Standardized Plume Flowfield) calculations were carried out to determine the composition of the gas mixture resulting from the hot exhaust gases flowing into ambient air, one late in the flight when the ambient pressure was 10 torr (Case I), and one earlier in the flight when ambient pressure was 1 atm (Case II). The following discussion considers two fuel gases,  $H_2$  and  $CO$ , mixing with  $O_2$  and diluent (all the other gases are considered to be diluents equivalent to nitrogen).

In Case I, pressures are so low that  $CO$  is not flammable (see earlier discussion on  $CO$  flammability limits), and we therefore treat the gas as a single fuel ( $H_2$ ) in  $O_2$ -diluent. Figure 14, a modification of Figure 4, shows the flammability limits for  $H_2$  in mixtures of  $N_2$  and  $O_2$  at 1 atm and various temperatures. The graph shows that the upper limits lie on lines of constant  $O_2$ , as suggested earlier. On the graph, a line has been drawn that shows the evolution of the mixture composition characteristic of Case I. It starts at the point labeled 361 K, at which hot gas (25% of which is  $H_2$ ) mixes with air (of which 78% is  $N_2$  and 22% is  $O_2$ ) and dilutes to pure air at 589 K. The initial and final phases of this expansion lie outside the limits of flammability, but in between the mixture will be flammable, almost regardless of the temperature. From the limits of auto-ignition for  $H_2$ - $O_2$ - $N_2$  shown on Figure 4, it is apparent that the gas will not ignite of its own accord, even at its hottest temperature. However, this does not rule out the possibility of ignition by contact with some hot surfaces.

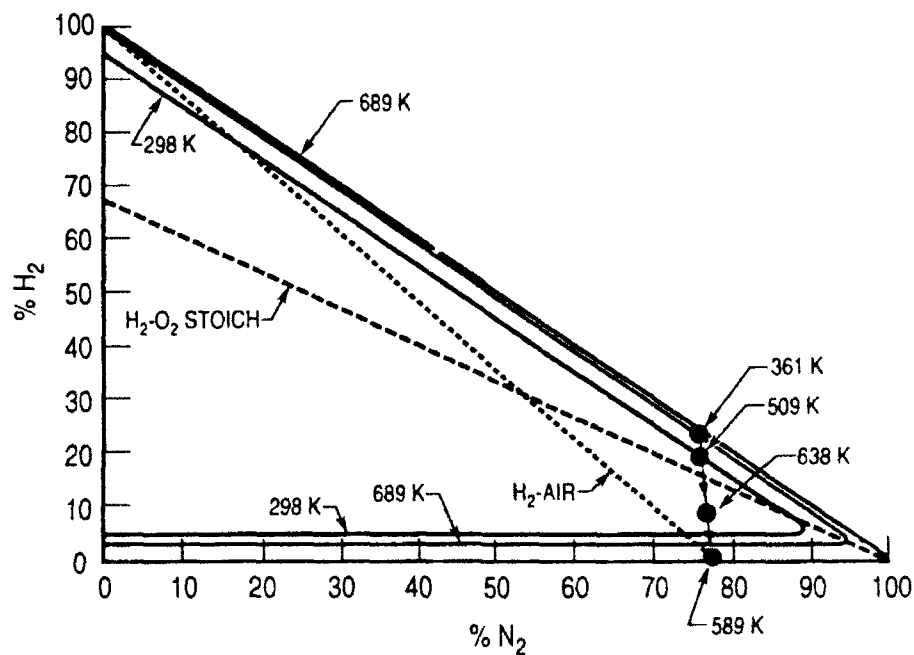


Figure 14. Flammability limits for  $H_2$ ,  $N_2$ , and  $O_2$ . Points show trajectory of Atlas leak at 10 torr ambient, assuming  $H_2O$ ,  $CO$ , and  $CO_2$  are all inert.



For Case II, the CO must also be considered a flammable gas, and the flammability limits are somewhat, but not greatly, different. Figure 15 shows calculated flammability limits for the exhaust mixture, which consists of 25% H<sub>2</sub>, 32% CO, and diluent. Flammability limits are shown only at 298 K for simplicity; as T increases, the limits will widen slightly, as in the preceding case. The "trajectory" of the expanding exhaust gas now looks somewhat different from Case I, but the conclusion is the same: after passing through a regime of insufficient O<sub>2</sub> to burn, the mixture will become flammable until the fuel gas is so diluted that it passes below the lower limit.

### SUMMARY

While a precise calculation of the flammability limits of H<sub>2</sub>, CO, or a mixture of the two depends on several parameters, Figure 4 shows that H<sub>2</sub>, at almost any temperature and 1 atm pressure, has very wide limits, so that knowledge of precise pressure, temperature, and composition is probably not necessary. In particular, one should note that, in contrast to most fuels listed in Table 4, the upper flammability limit of H<sub>2</sub> is nearly 100%—it is practically impossible to have a H<sub>2</sub>-oxidizer mixture too fuel-rich to burn. Detonation limits are more difficult to predict, but in any case flammability (deflagration) itself can result in considerable damage from temperature and pressure rise, and is itself, therefore, cause for concern.

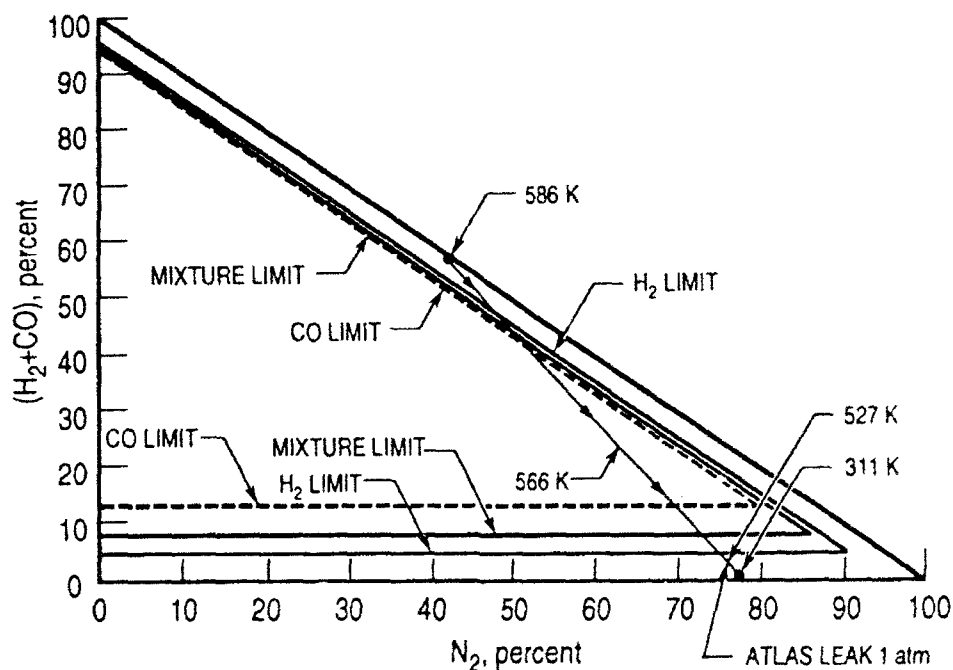


Figure 15. Flammability limits of  $H_2$ -CO mixture-- $H_2CO = 25:32$ , 298 K, 1 atm. Trajectory shows Atlas leak at 1 atm.

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